



Intergranular Cracking in High-Strength, Cold-Rolled, and Precipitation-Hardened Austenitic Stainless Steel UNS S35500

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Abstract

When quench annealed, stainless steel UNS 35500 (C 0.12, Cr 15.5, Ni 4.5, Mo 3, N 0.1%) is austenitic and soft. In cold-rolled and tempered condition, heavy cold rolling followed by precipitation hardening considerably strengthens the material (UTS 220 ksi [1517 MPa], elongation 10%). Its strength, combined with good corrosion resistance, makes the material attractive for use in critical load-bearing applications. In one application, helicopter rotor blades are attached to the drive shaft with a component strap pack, assembled from 0.014-in (0.36 mm)-thick laminae of the material. Premature fatigue failures of strap packs have occurred starting from intergranular cracks in single laminae. Chloride salts were detected at crack origins. This intergranular stress corrosion cracking was reproduced under crevices in slow-strain-rate tests conducted in 3.5% NaCl solution at 0.1 V (Ag/AgCl 4M KCl). The potential is typical of those attained by the material under thin, chloride-bearing condensate films exposed to air. Cracking did not occur when crevices were absent. Electrolytic polishing in chloride-free acids, combined with a standard overpassivation treatment in nitric acid, improved the resistance to crevice corrosion. This treatment slowed but did not prevent the onset of stress corrosion cracking (SCC) in slow-strain-rate tests conducted with an artificial crevice on the specimen surface.

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1. Introduction

Stainless steel UNS S35500, commonly known as AM355 steel, has the composition C 0.12, Cr 15.5, Ni 4.5, Mo 3, and N 0.1%. Quench annealed from 1900° F (1038° C), the steel is soft and almost completely austenitic with small (<5%) amounts of δ -ferrite. Heavy cold-rolling will considerably strengthen the steel because of an accompanying martensitic transformation. Further strengthening may be achieved with precipitation of fine carbides during a tempering treatment. Thus, with a 30% cold roll and a 850° F (445° C) temper, the strength is raised from 1030 MPa (150 ksi) to 1510 MPa (220 ksi). At 10% elongation, the cold-rolled and tempered (CRT) material is still very ductile. The carbides precipitate predominantly within and along martensite laths within the previously austenitic grains because of the high energy associated with these regions, and not selectively along austenitic boundaries as might happen in an annealed or mildly work-hardened austenitic stainless steel. Consequently, sensitization due to chromium depletion along grain boundaries is claimed not to be a problem [1]. The combination of high strength, ductility, and good corrosion resistance, due to its 15% chromium content, make this material a good candidate for structural service in military aircraft often used in corrosive marine atmospheres. In one such application, the propeller blades of a helicopter are attached to the rotor shaft via a flexible strap pack assembled from 23–27 laminae of CRT UNS S35500 steel only 0.014 in (0.36 mm) thick. In service, the strap pack experiences high alternating stresses and bending moments and is also exposed to the elements. Fractures of individual laminae have been observed during routine inspections, and one failure has occurred in service. Examinations of the fracture surface of broken laminae showed that the fracture had resulted from fatigue but that the fatigue cracks themselves had possibly started from intergranular cracks. Further, chloride ions were detected at crack origins [2]. Figure 1 shows a fatigue crack observed in a strap-pack lamina after 200 hr of flight time in a marine location.

The work reported here was performed to understand the mechanism of intergranular cracking and to find means of preventing it. Not much information is available on the structure and corrosion resistance of S35500 steel. Intergranular cracking was observed in precracked

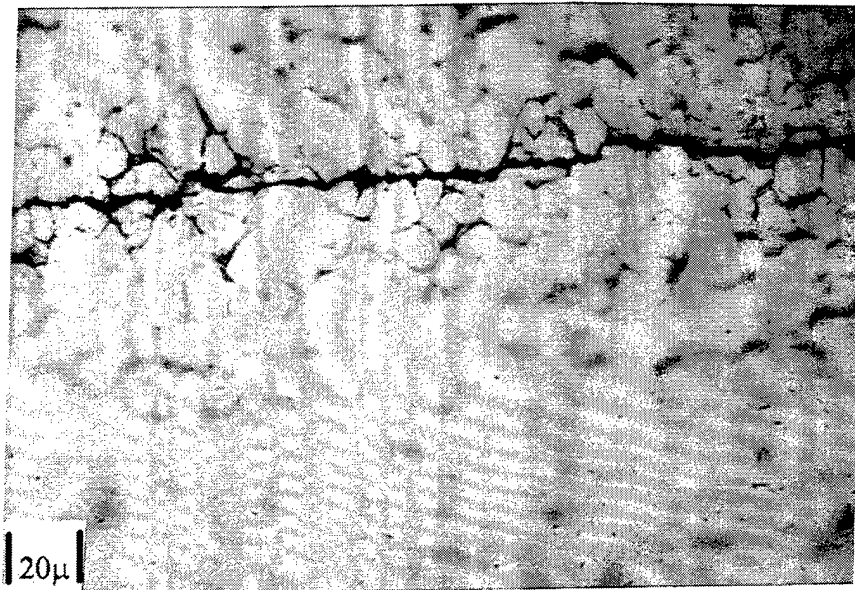


Figure 1. Fatigue Crack in a UNS S35500 Strap Pack Lamina After 200 hr Service in a Marine Environment.

fracture-toughness specimens of hardened steel exposed to a coastal atmosphere and to 20% NaCl solution [3]. An earlier publication claimed that material tempered at 1000° F (538° C) with a hardness of R_C 40 was immune to SCC in a 7000-hr salt-spray exposure [4]. In the absence of much helpful information in open literature on stress corrosion cracking (SCC) of the material, the presence of chlorides on the fracture surface of field-failed laminae and the intergranular appearance of the fracture surface at the beginning of fatigue cracks strongly suggested that the mechanism was similar to that of chloride cracking in other austenitic stainless steels. Austenitic stainless steels (e.g., steels UNS S30400 and S31600) crack transgranularly in neutral chloride solutions containing more than 100 ppm chloride [5] at temperatures above 140° F (60° C). Further, if the steel is sensitized, the cracking is intergranular. In sensitized S30400 steel, intergranular cracking occurred at room temperature [6, 7] when specimens were anodically polarized in 1 N sulfuric acid to a potential of 0.15 V SHE. This potential is probably in the active-passive transition region, based [8] on data for 194° F (90° C), and rules out hydrogen embrittlement as the cause of the cracking.

In the case of the cracking in strap-pack laminae, moisture condensing on laminae in a marine environment would become enriched in chlorides on evaporation of the water. Acidification would occur in pits or crevices [9], creating an environment conducive to intergranular stress corrosion. High residual stresses would already be present in the cold-rolled and tempered laminae of the strap pack. Superimposed on these would be the high stresses in service. The objective of the experimental program was therefore to find out if the intergranular cracking in the field could be reproduced in the laboratory in a chloride solution at potentials possible under aerated conditions. A solution containing 3.5% NaCl was chosen for all experiments. A large body of data exists for behavior of austenitic stainless steels in this solution, and it was thought that the choice of this solution would not only present a representative chloride environment but would also help comparison with results available for pitting and crevice corrosion behavior [10] of more highly alloyed austenitic stainless steels such as UNS S30400 and S31600.

The experimental program consisted of the following measurements on CRT S35500 steel specimens cut from strap-pack laminae: (1) Corrosion potential, E_{corr} , measurements in aerated 3.5% NaCl solution to determine the most noble (positive) potential the material could reach in this solution; (2) Cyclic polarization scans in the chloride solution to evaluate the pitting and crevice corrosion behavior of the material; (3) Stress corrosion cracking experiments in slow-strain-rate tests at an applied potential equal to the most noble potential measured in E_{corr} measurements (these experiments were conducted with and without an artificial crevice on the immersed specimen surface); and (4) Evaluation of selective surface treatments consisting of mechanical or electrolytic polishing with or without a subsequent overpassivation treatment in nitric acid on pitting, crevice corrosion, and SCC behavior in the chloride solution. Details of experimental procedures are provided in the following section.

2. Experimental Procedures

2.1 Materials. Specimens for tests were cut from 14 different strap-pack laminae, 0.36 mm (0.014) in thick. Some of these had seen field service, others had not. Some came from original

factory-made CRT strip that had not undergone sizing, edge smoothing, straightening, and other operations that happen before the strip is cut into laminae for a strap pack. A typical microstructure for these materials in the longitudinal direction is shown in Figure 2. It shows fine carbide precipitation across prior austenitic grains $\sim 25\text{ }\mu\text{m}$ in size. All these materials satisfied the manufacturer's specifications for CRT UNS S35500 steel for composition and mechanical properties (UTS - 220 ksi [1517 MPa], yield strength 200 - ksi [1379 MPa], elongation - 10%, and hardness - R_c 45). The specifications also required that the material have a 168-hr resistance to cracking in salt-spray chamber [11] at 70% UTS. There were differences in the surface microstructure of these different source materials, but differences in corrosion behavior were insignificant for tests described in this report. Specimens of the desired size were sheared from laminae for the tests.

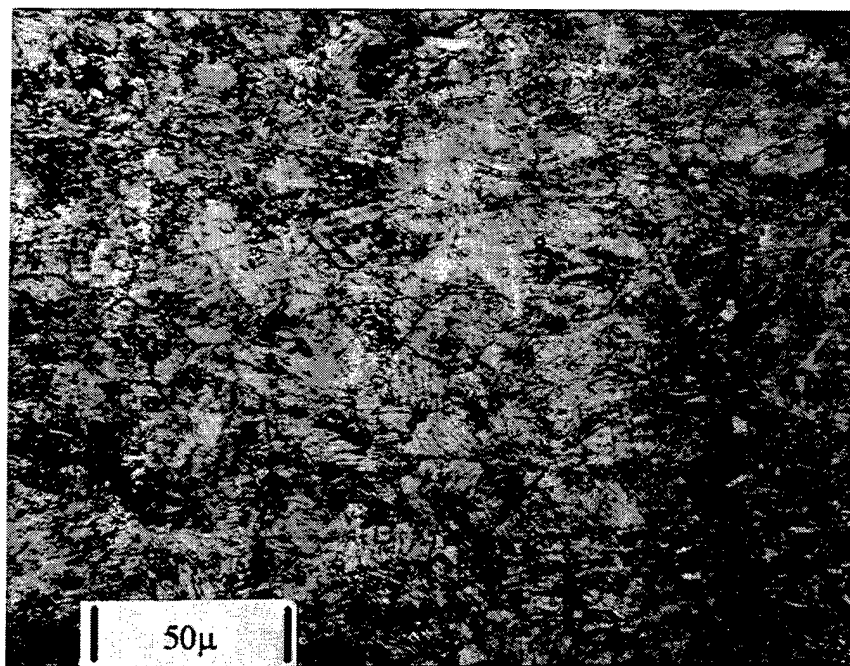


Figure 2. Microstructure of Cold-Rolled and Tempered UNS S35500 Steel Used for Strap Packs.

2.2 E_{corr} Measurements. Specimens sectioned from all 14-source strap-pack laminae were individually immersed in 3.5% NaCl solution continually sparged with laboratory-grade compressed air. Before being immersed, the specimens were repeatedly rinsed in deionized (DI)

water and ethyl alcohol to remove any grease, dirt, or soluble salts on the surface. The immersed surface area was $\sim 20 \text{ cm}^2$ (a $2 \times 5\text{-cm}$ panel with both sides exposed). The specimen was immersed in solution for 10 min before E_{corr} measurements were started against a silver/silver chloride (4M KCl) electrode. The measurements were made every 10 s for a period of 15-min using a CMS 100-electrochemical system.* All tests were performed at room temperature ($68\text{--}72^\circ \text{ F}$, [$20\text{--}22^\circ \text{ C}$]).

2.3 Cyclic Potentiodynamic Polarization Measurements. Cyclic potentiodynamic polarization measurements were made on an area of $\sim 1 \text{ cm}^2$, left bare on a larger specimen that was masked off with a stop-off lacquer.† The long axis of the specimen was parallel to the rolling direction, to produce cracking in the transverse cross section, as in field cracking. A large platinum counter electrode, an Ag/AgCl (4M KCl) reference electrode, and a CMS 100 system* were used. The solution was deaerated with high-purity nitrogen for at least 4 hr before a scan was begun, and the sparging continued during the scan. The scan rate was 10 mV/min, and standard procedures were used. All tests were performed at room temperature ($68\text{--}72^\circ \text{ F}$, [$20\text{--}22^\circ \text{ C}$]).

2.4 Stress Corrosion Cracking Experiments. Stress corrosion cracking experiments were performed on a specimen with a gauge section of $9.5 \times 38.1 \times 0.36 \text{ mm}$ ($3/8 \times 1.5 \times 0.014 \text{ in}$). The specimen was held in a polyethylene cell containing the test solution (500 ml) and pulled at a rate of 10^{-6} s^{-1} . The solution in the cell was open to atmosphere. A platinum counter electrode was arranged around the entire gauge section. A reference electrode was immersed into the solution through the cell lid. All tests were conducted at an applied potential‡ of 0.1 V. This potential was chosen based on the results of E_{corr} measurements. The potential was applied using a CMS 100 system. In some experiments, an artificial crevice was formed at the center of the gauge section by holding two serrated nylon cylinders against the specimen sides with a rubber band in a manner recommended in [12]. The nylon cylinders were 12.7 mm ($1/2 \text{ in}$) in diameter

* Gamry Instruments, Inc., 734 Louis Drive, Warminster, PA 18974.

† Microshield, from Tolber Division, 220 W. 5th St., Hope, AK 71801.

‡ All potentials in this report are expressed with reference to the Ag/AgCl (4M KCl) electrode.

and equally long. The serrations consisted of multiple, 1-mm-deep parallel cuts made in one face with a hacksaw. The serrations were perpendicular to the long axis of the specimen in the tests. The applied load, temperature, current, and potential were recorded every 10 min using a data-acquisition system. All tests were performed at room temperature (68–72° F [20–22° C]).

2.5 Surface Improvement Experiments. Electropolishing of stainless steels has been claimed to improve their resistance to pitting [10, 13–14] and crevice corrosion [15], especially if accompanied by an overpassivation treatment in hot nitric acid [10, 13–14, 16]. The effect of electropolishing alone or combined with passivation on pitting, crevice corrosion, and stress corrosion cracking was investigated. Electropolishing was done in a phosphoric acid-sulfuric acid mixture [17] (150-ml water + 300 ml 85% orthophosphoric acid + 550-ml concentrated sulfuric acid) for 4 min at a current density of 0.3 A/cm². Overpassivation was performed in 50% nitric acid at 122° F (50° C) for 30 min [18]. All tests were performed at room temperature (68–72° F [20–22° C]).

3. Results

3.1 E_{corr} Measurements. Figure 3 shows a typical E_{corr} measurement over a 15-min period. It shows that the potential changed over a range of 80 mV and was, apparently, the result of a dynamic equilibrium between reduction and oxidation reactions over the immersed surface. The sharp transient in E_{corr} at about 200 s was apparently caused by the formation of a pit and its repassivation. Similar behavior was observed for all 12 samples taken from different laminae. However, the range of values over which E_{corr} changed over a 15-min period was different, even when samples came from different parts of a single lamina and had, presumably, seen the same processing and life history. The lowest E_{corr} value was -0.283 V and the highest, 0.092 V. On the basis of these results, it was concluded that the value of 0.1 V was the most positive that this steel might attain in aerated 3.5% NaCl solution, and all stress corrosion tests were done at an applied potential of 0.1 V.

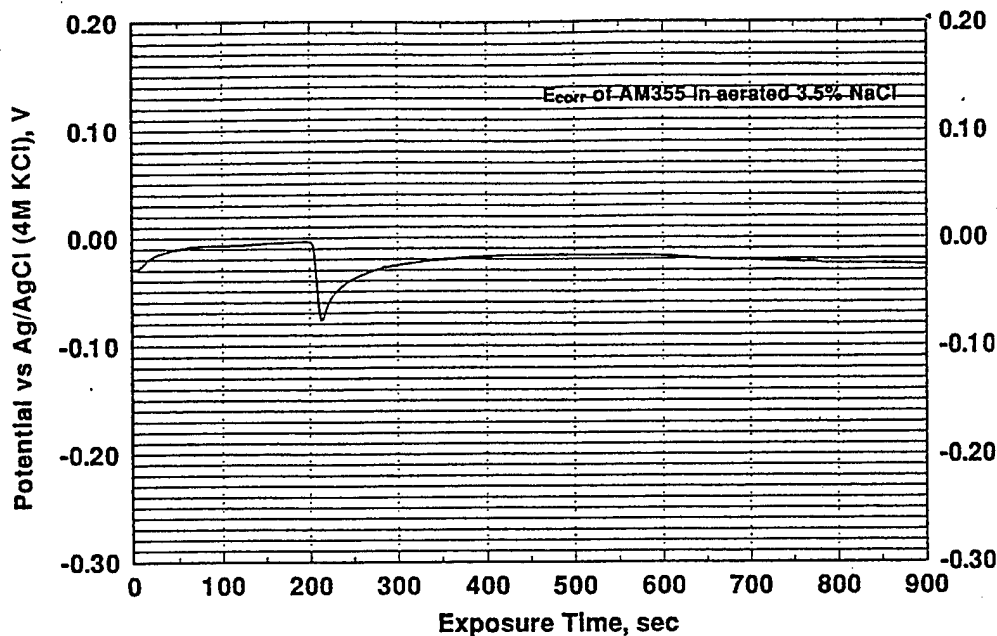


Figure 3. Typical E_{corr} vs. Time Change for UNS S35500 in Aerated 3.5% NaCl.

3.2 Potentiodynamic Polarization Measurements. Figure 4 shows a typical polarization curve obtained in deaerated 3.5% NaCl on a specimen cut from a strap-pack lamina. It is seen that pitting did not begin until a potential of 0.24 V was reached, and that the protection potential, E_{prot} , was -0.29 V. The figure also shows the E_{corr} range, -0.16 to -0.04 V, measured in aerated solution for the same sample. It is seen that the E_{corr} range was well above E_{prot} . As in the case of the E_{corr} measurements, the polarization plots were similar for all 12 different specimens, but the pitting potential value varied over a wide range, 0.01 to 0.46 V, even for samples that came from different areas of the same strap-pack lamina. The E_{prot} range was, on the other hand, narrower, -0.16 to -0.29 V. In all cases, E_{corr} values measured on the same sample in aerated solution were more than 0.1 V more positive than E_{prot} , indicating a strong likelihood of pitting and crevice corrosion.

3.3 Stress Corrosion Cracking Experiments. No cracking was observed on uncreviced specimens tested in the freely corroding state or at applied potentials of 0.05 or 0.1 V, the only two applied-potential conditions tested. Figure 5 shows change in stress and total current with

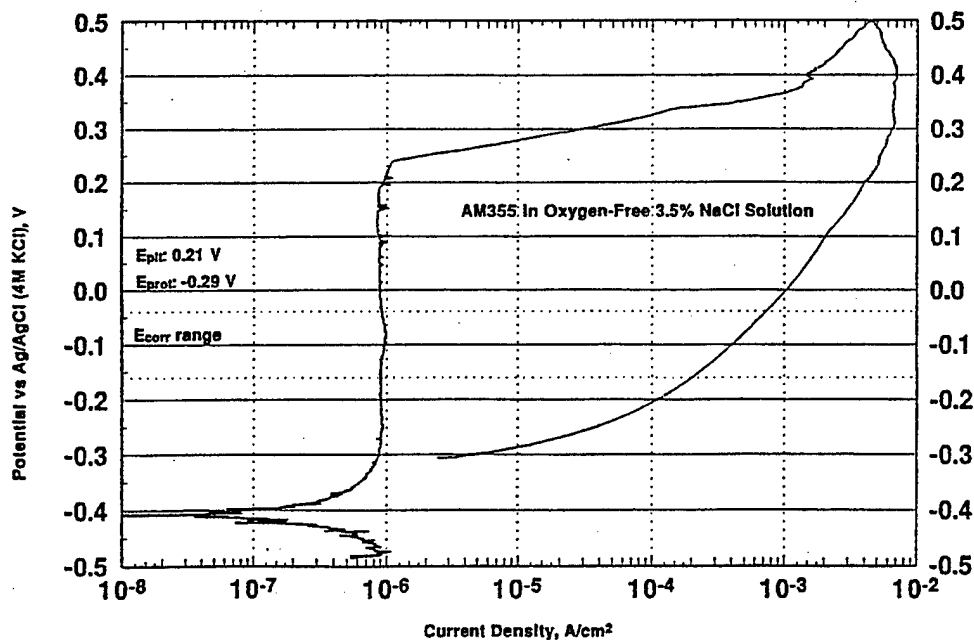


Figure 4. Typical Polarization Curve Obtained on S35500 Strap-Pack Steel in Deaerated 3.5% NaCl.

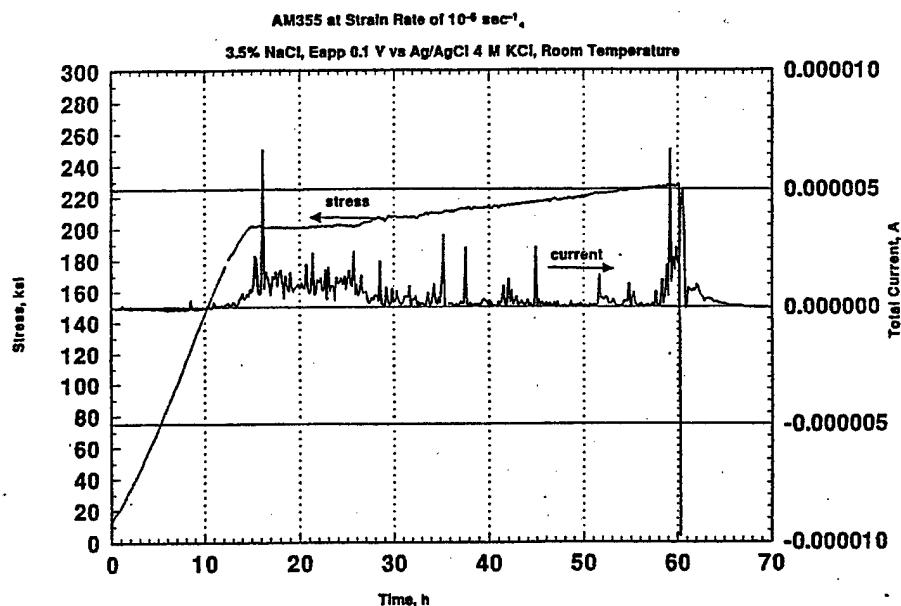


Figure 5. Stress and Current in Slow-Strain-Rate Test on Cold-Rolled and Tempered S35500 Steel in 3.5% NaCl at 0.1 V and 10⁻⁶ s⁻¹.

time at 0.1 V applied potential in the absence of a crevice. There was no cracking, and the specimen had an elongation of 15%, tensile strength of 1524 MPa (222 ksi), and yield strength of 1373 MPa (200 ksi). These values were similar to those obtained in an air test. The current was anodic but small ($<5 \times 10^{-7}$ A/cm²) over most of the test, indicating that the test material was in a passivated condition. The lack of cracking was confirmed by the ductile nature of the fracture surface, as revealed in microscopic examination.

However, cracking occurred under these conditions if crevice conditions were created on the specimen surface by placing an artificial crevice-former on the specimen surface. Data from one such test are shown in Figure 6. It is seen that time to failure decreased from 60 hr without crevices to less than 10 hr with crevices and the maximum stress sustained was only 1030 MPa (150 ksi), well below the yield strength of the material. The data also show that the total current increased sharply at 5 hr and stayed at a relatively high 0.75 mA until fracture occurred. At the moment of fracture, the current dropped sharply, to ~0.15 mA, but continued to be anodic and at a level higher than the current before the onset of cracking. During cracking, new intergranular material is being exposed to the solution. When cracking has progressed to such an extent that the load borne by the intact segment exceeds the strength of the material, this remaining material fails in a ductile mode. The resulting fracture surface is therefore a mixture of intergranular and ductile, dimpled fracture. The large current during cracking suggests that the intergranular regions being dissolved are chemically much more active to the changed solution chemistry in the crevice than the ductile-cum-intergranular fracture surfaces exposed to the same solution after complete fracture. Secondary cracks were not observed.

Part of a fracture surface showing its intergranular and dimpled areas is shown in Figure 7. In the picture, intergranularly fractured areas flank an area of dimpled fracture. Further, one of the two intergranular areas shows greater corrosion damage, showing that: (1) the fracture here occurred earlier in time, and (2) the solution to which it was exposed was more corrosive to bulk metal than the bulk solution.

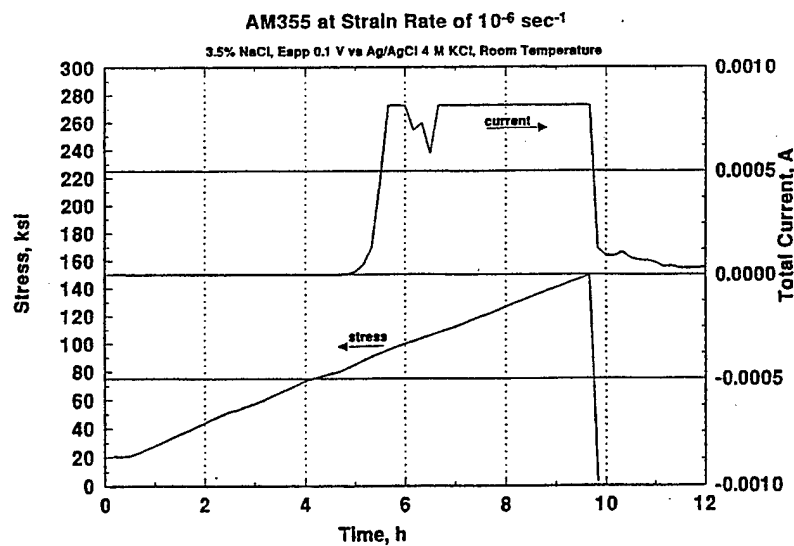


Figure 6. Stress and Current in Slow-Strain-Rate Test on Cold-Rolled and Tempered S35500 Steel in 3.5% NaCl at 0.1 V and 10^{-6} s^{-1} With an Artificial Crevice on the Gauge Surface.

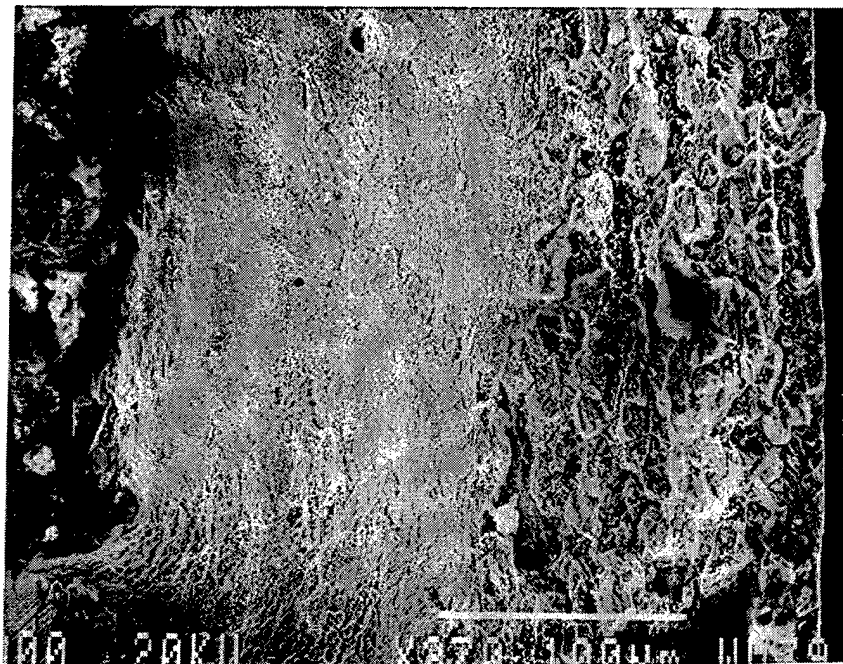


Figure 7. Mixed Fracture Surface of S35500 Specimen Tested With Artificial Crevice at 0.1 V and 10^{-6} s^{-1} .

In this test, judging from the change in current (Figure 6) cracking seems to have begun when the stress was ~80 ksi in the fifth hour of straining (the straining would have otherwise proceeded for a total of ~60 hr had SCC not occurred). The stress level at which cracking started was different for a total of five tests in which cracking occurred under crevice and ranged from 150 to 230 ksi. The corresponding time to failure ranged from 9.8–19.2 hr.

3.4 Surface Improvement Experiments.

3.4.1 Polarization Behavior. Electropolishing improved the corrosion performance of S35500 steel in 3.5% NaCl. However, the improvement did not occur until at least the top 0.5 mil (13 μm) of material had been removed. It is likely that repeated heating during processing of the CRT material in the manufacture of laminar material results in chromium depletion at the surface, as is known [19] to occur in the case of 18-8 type stainless steels. Apparently, this outer, chromium-depleted material needed to be removed in electropolishing before its corrosion performance could improve. Removal, in electropolishing or pickling, of nonmetallic inclusions, especially sulfide inclusions, has also been shown [20] to lead to an improved pitting resistance in stainless steels. Figure 8 is a polarization curve obtained in deaerated 3.5% NaCl on electropolished steel. It is seen that any hysteresis in current that would indicate pitting is absent. When material that was both electropolished and overpassivated was to a similar cyclic potentiodynamic polarization (data not presented graphically in this report), hysteresis was again absent, E_{corr} was more noble (0.33 V vs. 0.04 V in Figure 8), and both anodic and cathodic branches were displaced to the left and lower current densities. Thus the electropolished and overpassivated material was even more resistant to pitting than material that was only electropolished.

3.4.2 Crevice Corrosion. When material under a serrated PTFE (Teflon) washer was held at 0.1 V in deaerated 3.5% NaCl solution, as-received material quickly developed active crevice corrosion. Material from which the top 0.005 mil (13 μm) had been removed mechanically, electrolytically, or removed electrolytically and then passivated in nitric acid, was increasingly more resistant.

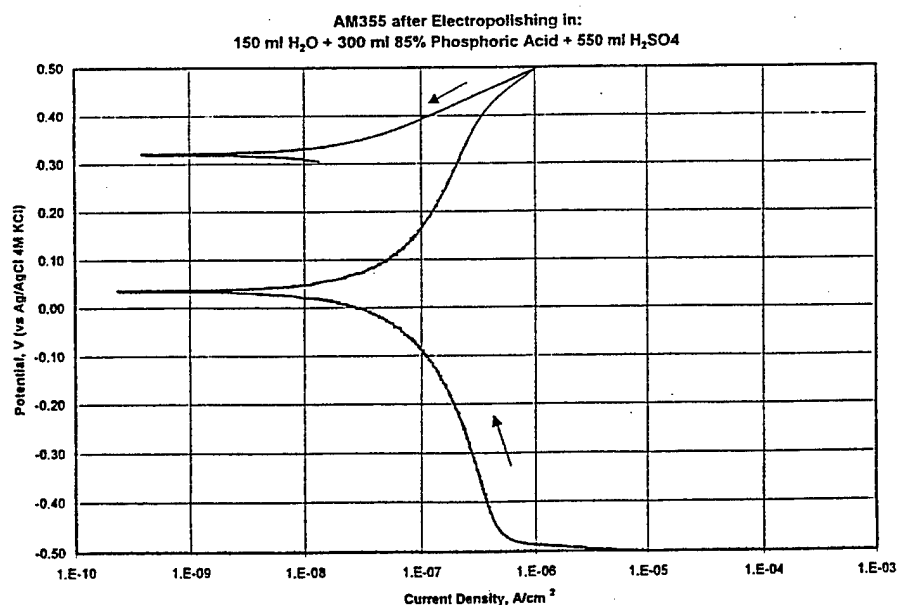


Figure 8. Polarization Curve for Electropolished S35500 Strap Pack Steel in Deaerated 3.5% NaCl.

The change in current with time for crevice assemblies with these four different types of surface treatments is shown in Figure 9. The current under the crevice assembly increased in a seemingly runaway manner for the as-received material. Examination of the specimen after a 20-hr test showed heavy attack under the crevice. On the other hand, current for electropolished and passivated material showed no increase over a nearly negligible passivation current ($<1 \times 10^{-7}$ A) for 30 hr and continued to do so for a total of 300 hr of test (data not shown in Figure 9). Intermediate behavior was observed in only abraded and only electropolished materials. These latter materials showed an increase in current after the 5th and 14th hr, respectively, but to a much lower final total current of 5×10^{-4} A, vs. 0.005 A for the as-received material. Examination of these latter specimens after a 23-hr test showed only pits under the artificial crevices—not heavy crevice corrosion. It is thus seen that electropolishing combined with overpassivation led to a considerable improvement in the pitting and crevice corrosion resistance of CRT S35500 steel.

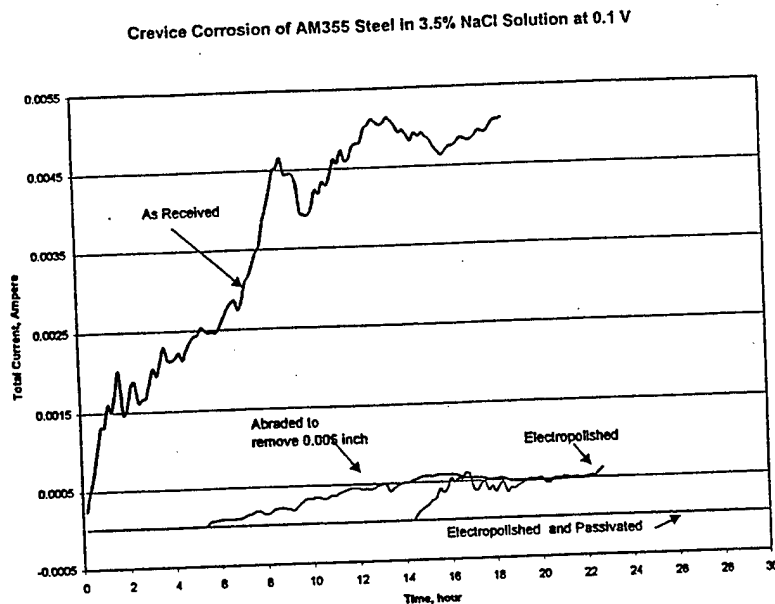


Figure 9. Current for Creviced, S35500 Strap Pack Steel at 0.1 V in Deaerated 3.5% NaCl for Different Surface Conditions.

3.4.3 Stress Corrosion Cracking. Figure 10 shows change in stress and current when an electropolished, overpassivated, and creviced specimen was strained at 0.1 V in a slow-strain-rate test. Premature failure by intergranular cracking did occur, but the time to failure, 24.5 hr, was longer and the maximum stress sustained, 250 ksi, was much higher than when as-received material was strained under similar conditions. Figure 11 is a scanning and electron microscope (SEM) photograph of the crack origin in the crevice area showing both the fracture surface and the free surface near the crack origin. It shows cracks originating from an area of crevice corrosion on the specimen surface. These results, Figures 10 and 11, show that in an electropolished and overpassivated condition, the material was resistant, but not immune, to chloride cracking under crevice conditions.

4. Discussion

4.1 Mechanism of Intergranular Cracking. The results of electrochemical tests presented earlier show that S35500 steel in the CRT condition is prone to pitting and even more so to

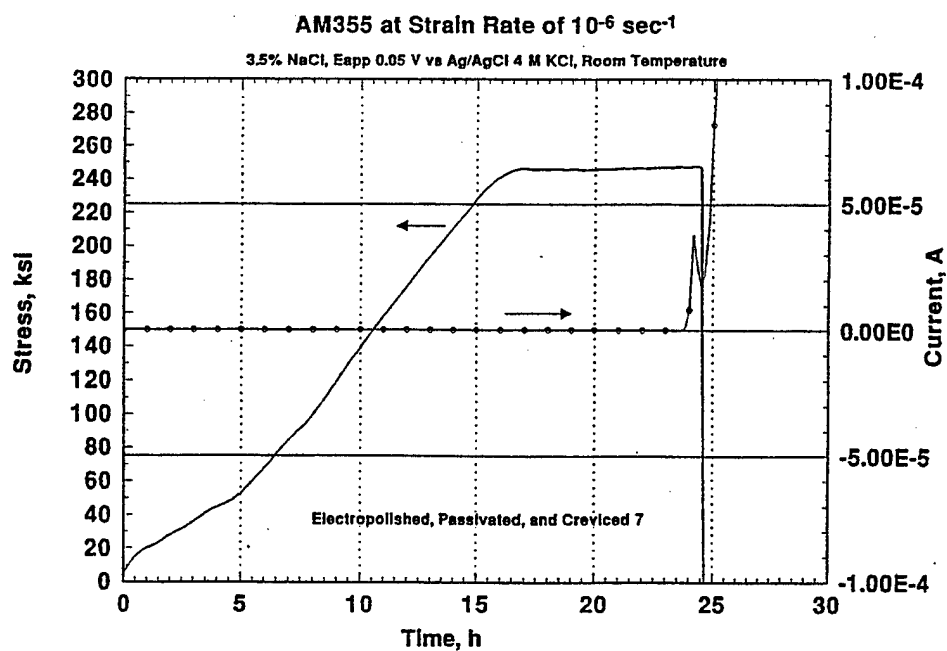


Figure 10. Data for Slow-Strain-Rate Test of Electropolished, Creviced Specimen Held at 0.1 V in 3.5% NaCl.

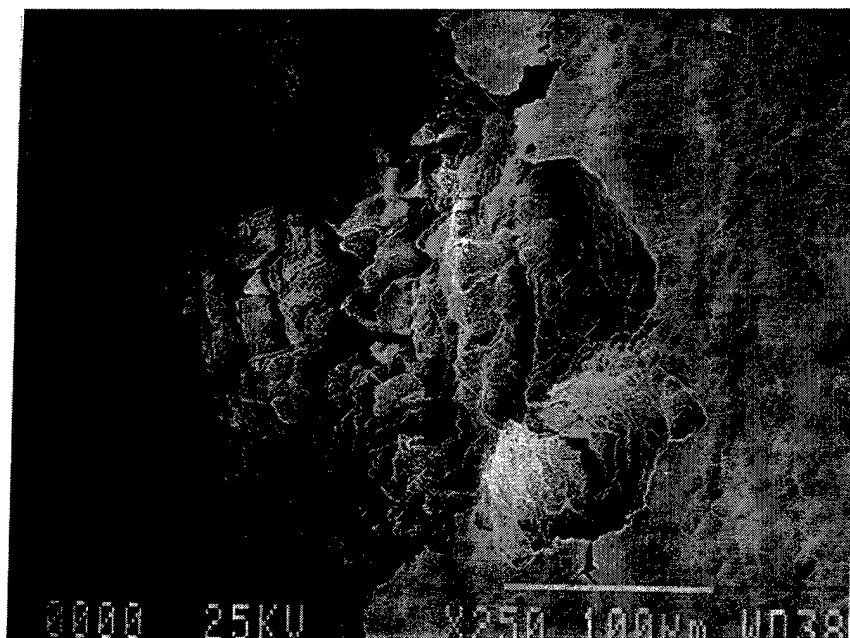


Figure 11. SEM Photograph of the Origin of Intergranular Stress Corrosion Cracking in an Electropolished and Overpassivated Specimen in a Slow-Strain-Rate Test.

crevice corrosion in chloride solutions. In Figure 9, the current is small even after pitting had been initiated for abraded or electropolished samples. On the contrary, current was increasingly large for the as-received sample once crevice corrosion had been initiated. These results show that pits on this material in chloride solution may get repassivated and stop growing, but crevice corrosion, having once begun, continues at an increasing rate. Once crevice corrosion has begun, consequent and ever-increasing acidification of the crevice solution [21] eventually causes stress corrosion cracking in the presence of sufficiently high tensile stresses. The third requirement, that of a structure susceptible to SCC, is apparently satisfied: S35500 steel in the CRT condition seems to have a sensitized structure similar to the one occurring in sensitized, higher-alloy, austenitic stainless steels. The tempering treatment is, after all, conducted for the purpose of carbide precipitation. The tempering temperature, 850° F (445° C), is below the range, 950–1450° F (510–788° C), in which sensitization of austenitic stainless steel is generally considered [21] to occur. So, slow diffusion of chromium, which leads to chromium depletion in the vicinity of carbides in a sensitized stainless steel, will be even more of a sensitization factor in the case of the present material.

4.2 Preventive Measures. The results presented earlier show that electropolishing combined with a nitric acid overpassivation treatment led to a considerable improvement in the crevice corrosion resistance of the present test material. Electropolishing removes nonmetallic inclusions at the surface as well as other surface blemishes that might serve as initiation sites for pitting and crevice corrosion. Note that a top layer of more than 12 μm (0.0005 in) needed to be removed before better corrosion resistance was observed. This may be because, beyond the removal of surface blemishes, cold-worked areas, and inclusions, a low-chromium skin resulting from processing, probably also needed to be removed.

The improved corrosion resistance of electropolished material from overpassivation (Figure 9) is striking. Improvements from such surface treatments have been dismissed as [22] artifacts. However, the improvement in pitting and corrosion resistance in Figure 9 was no "artifact." The improvement was verified in multiple tests using different acids for

electropolishing. The improvement was accompanied by a more noble E_{corr} . It is therefore possible that the improvement occurs due to enrichment of the passive layer with chromium, as claimed in recent literature [23]. It is likely that, if the experiment of Figure 9 had been continued beyond 300 hr, crevice corrosion would have begun eventually under the serrated washer. It is also possible that results would have been different for a different crevice geometry. However, the improvement on electropolishing and nitric-acid overpassivation of S35500 strap-pack steel in its resistance to pitting, crevice corrosion, and stress corrosion is considerable and is expected to improve corrosion, stress corrosion, and fatigue performance of strap packs in marine environments.

5. Conclusions

- (1) Precipitation hardened, cold rolled and tempered, semiaustenitic stainless steel UNS S35500 showed intergranular stress corrosion cracking when creviced specimens were tested in 3.5% NaCl solution at 0.1 V at a strain rate of 10^{-6} s^{-1} . This material may attain an electrical potential as high as 0.1 V if covered with a thin film of seawater.
- (2) Surface treatment of the material consisting of removal of the top 13- μm layer of the material by abrasion or electropolishing followed by overpassivation in nitric acid improved the pitting and crevice corrosion resistance of the material in 3.5% NaCl solution considerably. Material so treated was more resistant, but not immune, to stress corrosion cracking under a crevice.
- (3) Nitric acid overpassivation, such as a 30-min treatment in 50% nitric acid at 122° F (50° C), after removal of a top 13- μm layer by electropolishing, is a treatment recommended to improve the fatigue performance of strap packs of this material in the field.

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